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Direct Hydrogenation of Plant Oils to Alkanes at Low Temperatures and Pressures using Pt and Pt-Re Supported on TiO₂ Catalysts

Amin S. ALIKASTURI¹, Haresh G. MANYAR¹, Gary N. SHELDRAKE¹, Christopher HARDACRE^{1,*}

¹*CenTACat, School of Chemistry and Chemical Engineering, Queen's University Belfast, David-Keir Building, Stranmillis road, Belfast BT9 5AG, UK.*

**corresponding author: c.hardacre@qub.ac.uk*

Introduction

Rapid depletion of fossil fuels and stringent regulations curbing CO₂ emissions necessitates the use of renewable natural resources for liquid fuel production. In this context, direct hydrogenation of plant oil based natural triglycerides and fatty acids into valuable hydrocarbons is a potential substitute for production of drop-in biofuels [1-3]. Direct hydrogenation of plant oils to bio fuels is an attractive alternative to transesterification of triglycerides (FAMES) due to various issues related to stability, unfavourable cold flow properties and engine compatibility issues of FAMES. However, current manufacturing processes are expensive and hazardous requiring very high pressures and temperatures (200-400 bar hydrogen, 200-400 °C). Under these conditions, control of the selectivity to the desired hydrocarbons is difficult. In this study, we have achieved catalytic hydrogenation of triglycerides at remarkably low temperatures (60-130 °C) and hydrogen pressures (5-30 bars) to corresponding alkanes and alcohols using monometallic 4%Pt/TiO₂ and bimetallic 4%Pt-4%Re/TiO₂ catalysts. It was possible to tune product selectivity to either hydrocarbons or long chain alcohols. Tristearin was chosen as a model triglyceride, since it is abundant in most vegetable oils, to investigate the reaction pathways and establish reaction kinetics for hydrogenation. Reaction pathways were also explored using stearic acid as the model substrate and the kinetic analysis indicated that a two-site Langmuir-Hinshelwood model with dissociative adsorption of hydrogen and surface reaction as the rate-controlling step fitted well to the experimental data. The kinetic model predicted reaction rates of hydrogenation of acid to alcohol, and subsequent dehydration of alcohol to alkane as well as decarboxylation of acid to alkane with excellent reliability.

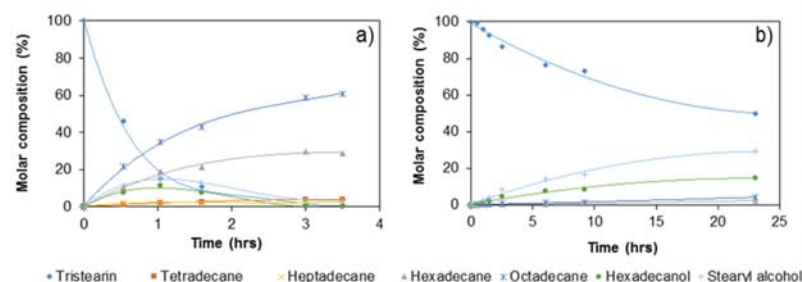


Figure 1. Reaction profile of hydrogenation of tristearin using (a) bimetallic 4wt%Pt-4wt%Re/TiO₂ catalyst and (b) monometallic 4wt%Pt/TiO₂ catalyst; Reaction conditions: temperature 130 °C, hydrogen pressure 20 bar, speed of agitation 1500 rpm, catalyst loading 0.5g, tristearin 1.4g, cyclohexane 40 cm³.

Results and Discussion

A typical reaction profile of the hydrogenation of tristearin using bimetallic 4%Pt-4%Re/TiO₂ and monometallic 4%Pt/TiO₂ catalysts at 130 °C and hydrogen pressure of 20 bar is shown in Figure 1. In presence of bimetallic 4%Pt-4%Re/TiO₂ catalyst, high selectivity to alkanes (99%) with complete conversion of tristearin was obtained, while in presence of monometallic 4%Pt/TiO₂ catalyst, high selectivity (91%) to corresponding alcohols was achieved. The scope of the liquid phase hydrogenation using both monometallic and bimetallic catalysts was further extended to a variety of plant oil feedstocks such as sunflower, rapeseed, soyabean, olive, coconut, corn and palm oils, as shown in Table 1. A broad range of natural triglycerides were successfully hydrogenated to corresponding alkanes in the C₁₀-C₁₈ range, which can be readily exploited for fuel blending purposes. The most notable exception being found with coconut oil which formed mixture of C₇-C₁₈ alkanes as the major product irrespective of whether 4wt%Pt/TiO₂ and 4wt%Pt-4wt%Re/TiO₂ catalysts were employed.

Table 1. Hydrogenation of Plant oils under the reaction conditions in Figure 1.

Plant Oil	Catalyst metal/TiO ₂	Time/h	Plant Oil Conversion/%	Selectivity (%)	
				Alkanes	Alcohols
Tristearin	4%Pt-4%Re	3	100	99	1
Palm	4%Pt-4%Re	19	99	100	-
Sunflower	4%Pt-4%Re	7	73	93.4	6.6
Olive	4%Pt-4%Re	23	98	97.2	2.8
Corn	4%Pt-4%Re	5	71	86.7	13.3
Soyabean	4%Pt-4%Re	5	78	95.2	4.8
Coconut	4%Pt-4%Re	22	98	100	-
Rapeseed	4%Pt-4%Re	24	100	95.5	4.5
Tristearin	4%Pt	23	50.1	12.4	87.6
Palm	4%Pt	90	45.3	12.6	87.4
Sunflower	4%Pt	20	16.2	25.5	74.5
Olive	4%Pt	20	23.1	15.1	84.9
Corn	4%Pt	33	16.3	-	100
Soyabean	4%Pt	22	74.3	33.3	66.7
Coconut	4%Pt	90	22.2	100	-
Rapeseed	4%Pt	20	39.4	21.2	78.8

Significance

In summary, new efficient monometallic and bimetallic catalysts have been established for direct hydrogenation of plant oils to valuable long-chain hydrocarbons and alcohols under mild reaction conditions. At 130 °C and 20 bar hydrogen, high yield of long chain alkanes (95-100%) was achieved. It was possible to tune the product selectivity to obtain alkanes or alcohols by choice of catalysts used.

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